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ORIGINAL PAPER

Ultrafast removal of heavy metals by tin oxide nanowires as new adsorbents in solid-phase extraction technique

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Abstract In the present research, the removal of lead(II) and copper(II) from aqueous solutions is studied, using SnO_2 nanowires as new adsorbent on solid-phase extraction disk and compared with pine core and buttonwood as biosorbents. Batch adsorption experiments were performed as a function of pH, adsorption time, solute concentration and adsorbent dose for biosorbents. Also, the pH, transfer rate of solution and metal concentration were selected as experimental parameters for the removal of heavy metals by SnO_2 nanowires. All of the parameters were optimized by experimental design method for sorbents. The experimental equilibrium adsorption data are tested for the Langmuir and Freundlich equations. Results indicate the following order to fit the isotherms: Langmuir > Freundlich, in case of lead and copper ions. The removal of Cu(II) and Pb(II) was performed by selected sorbents in the presence of interferences ions. This led to no remarkable decrease in the removal efficiency of SnO_2 nanowires. Using the SnO_2 nanowires in the wastewater treatment indicated 96.8 and 85.28% removal efficiency in only 7 min for Pb(II) and Cu(II), respectively. SnO_2 nanowires were found as reusable sorbent. Therefore, SnO_2 nanowires have a good potential for application in environmental protection.

Keywords Factorial design · Isotherms · SnO_2 nanowires · Solid-phase extraction · Ultrafast heavy metal removal

Introduction

Heavy metal pollution has become one of the major threats to the environment due to their toxicities, non-biodegradability, bioaccumulation in human body and food chain and most likely carcinogenicities to human (Stafiej and Pyrzynska 2007). Accumulation of heavy metals in the environment causes heavy metal poisoning even when they are present in low concentrations (Hsieh and Horng 2007). The major source for heavy metal contamination of aquatic environments is industrial activities such as refining, painting, metal plating and cleaning, battery and car radiator manufacturing, textile and leather tannins (Rao et al. 2007; Shahidi et al. 2016; Simonovic et al. 2007; Toprak and Girgin 2000). Lead, copper, mercury, chromium, arsenic, cadmium, zinc and nickel are the most common contaminants found in environmental water samples (Rao et al. 2007). Pb(II) and Cu(II) are the metal ions that are used most widely in industry. In the recent years, it is of vital importance to determine and identify lead and copper ions because of high toxicity. They can cause a variety of negative effects on human health, for example, neurotoxicity, jaundice, liver toxicity, anemia, encephalopathy, hepatitis and nephritic syndrome (Singha and Das 2012). The permissible limit of lead and copper was notified by

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World Health Organization as 10 μg l^{-1} and 1.5 mg l^{-1}, respectively (Goel et al. 2005). A wide variety of techniques were applied for the elimination of metal pollutants from aqueous solutions including ion exchange, reverse osmosis, membrane filtration, evaporation, solvent extraction and adsorption (Fu and Wang 2011; Kumar et al. 2017; Kamal et al. 2017). Among these existing techniques, adsorption was developed due to high yield, easy operation and the variety of adsorbents. However, in recent years due to the application of various biomaterials for the sorption purpose, the term adsorption has become more popular as biosorption. A number of biomaterials were widely employed for metal ion removal from aqueous solutions including agricultural wastes, biopolymers and plant wastes (Pan et al. 2009; Mishra et al. 1996). Phytoremediation has emerged as an environment-friendly technology that employs plants for the uptake of heavy metals (Boonyapookana et al. 2005). This technology involves growing plants on appropriate sites and application of dried powder of root, leaves or skin of plants in water (Weerasinghe et al. 2008; Lasat 2002). Development of nanotechnology introduced a new insight into sorbent for extraction of compounds or removal of pollutants (Alizadeh and Najafi 2013; Alizadeh et al. 2016; Alizadeh 2016). In recent years, the development of nanotechnology in preparation of sorbents has enhanced the efficiency of heavy metal removing. In this concern, metal nanostructures and nanocomposites including sodium titanate nanofibers, nanosized carbon immobilized alginate beads, nanomineral and nanoadsorbent prepared by incorporating organic ligand onto mesoporous silica were developed to improve the removal of heavy metals from environment (Li et al. 2011; Jung et al. 2015; Lata and Samadder 2016; Awual et al. 2014). The objectives of this study were to investigate the ability of SnO_2 nanowires as solid-phase extraction to accumulate Pb(II) and Cu(II) from water samples. Tin oxide nanowires have chemical, thermal and mechanical stability. Investigation of SnO_2 nanowires BET (Brunauer, Emmett and Teller) showed high surface area for nanowires that able to increase the adsorption efficiency of heavy metals (Kim and Cho 2008; Johari et al. 2012; Rikka et al. 2015; Tran and Rananavare 2011). Also, because of oxygen groups on the structure of nanowires, these wires are able to interact with heavy metals. The results were compared with pine core and buttonwood fruit powder as sorbent for phytoremediation process. Extraction conditions were optimized by experimental design for all of sorbents. The research was performed in the Qom University at the 2016 summer.

Materials and methods

Reagents and analytical standards

All analytical grade compounds such as nitric acid, ammonia, tin chloride(IV), copper sulfate, lead nitrate, chloridric acid and sodium hydroxide were purchased from Fluka (Buch, Switzerland). Stock solution of Pb(II) and Cu(II) was prepared by solving lead nitrate and copper sulfate in distilled water to 1000 mg l^{-1} and stored in dark place at 4 °C. Working solutions were prepared by dilution of standard stock solution.

Instrumentation

Determination of heavy metals was carried out by Varian AA220 (Mulgrave Victoria, Australia) atomic absorption spectroscopy instrument. The scanning electron microscopy (SEM), Philips (Bend, OR 97702, USA) XL30 instrument, was employed to confirm the morphology of tin oxide nanowires as well as to ensure the required size of SnO_2 nanowires as sorbent of SPE. Moulinex grinder (Germany) was used to mill pine core and buttonwood fruits. SnO_2 nanowires were separated from growth solution by Herolab centrifuge (Wiesloch, Germany) Hicen-21. LAWKIM vacuum pump (Shindewadi, India) was used as the controller of water flow rate from SnO_2 nanowires SPE disk.

Preparation of biosorbents

Pine cores and buttonwood fruits were supplied from Sirjan city. These biosorbents were washed two times by distilled water and were dried in the oven at 80 °C for 72 h. These were milled by a grinder separately and were categorized to three sizes of (<120, 150–250, >300 mm) by a standard size sieve.

Preparation of SnO_2 nanowires SPE disk

SnO_2 nanowires were prepared by modified Lupan method (Lupan et al. 2007). Briefly, a solution containing tin chloride ($SnCl_4.5H_2O$, 0.03 M) and ammonia (25% v/v) (ratio of 1:30) was employed for the growth of tin oxide nanowires. The solution was kept in the 95 °C for 15 min. Nanowires were deposited by centrifuge process at 15,000 rpm for 15 min. The nanowires were washed three times by distilled water and annealed at 300 °C for 5 min. Solid-phase extraction disk was prepared by fixing SnO_2 nanowires (1.68 g) on the Whatman filter paper in the filter holder which included sintered glass disk.

Procedure of heavy metal removal by biosorbents

Pb(II) and Cu(II) heavy metals were removed from water by pine core and buttonwood fruit, separately. In this investigation, different amounts (0.2–10 mg l^{-1}) of biosorbents powder at three different sizes (<120, 150–250, >300 mm) were added to 20 ml of heavy metal solution which contained 50 mg l^{-1} of Pb(II) and Cu(II). During extraction process, the solutions were shaken at 150 rpm. The pH of solution was set at the range of 2–8 by nitric acid and sodium hydroxide. After the extraction, the solution was passed through filter paper and biosorbent was removed from solution. AAS was applied for the determination of heavy metal residual in the water sample.

Procedure of heavy metal removal by SnO_2 nanowires SPE (SNW-SPE)

The removal of Pb(II) and Cu(II) was performed from 20 ml solution including heavy metals [10–90 mg l^{-1} of Pb(II) and CU(II)] at pH 4–10. The solution was passed through the SNW-SPE disk at different flow rates (1, 2, 4 ml min^{-1}). After extraction, heavy metal residuals were determined by AAS in solution. Finally, SNW-SPE was washed by 60 ml of nitric acid at pH = 2 as reusable SPE disk.

Optimization of removal parameters

The removal of Pb(II) and Cu(II) was performed using pine core and buttonwood fruit powder, separately. Four parameters including different amounts of powders (0.2–10 mg l^{-1}), different sizes of powders [<120 mm (1), 150–250 mm (2), >300 mm (3)], pH (2–8) and removal time (10–180 min) were optimized by the experimental design method. Stat Graphic plus 5.1 software was used to design 30 experiments via Box–Behnken method in order to achieve maximum removal efficiency of heavy metals.

Also, SNW-SPE disk was applied for removing the mentioned heavy metals from water solution. Like biosorbents, three parameters including pH (4–10), solution flow rate (1, 2, 4 ml min^{-1}) and heavy metal concentration (10–90 mg l^{-1}) were optimized by Box–Behnken method at three levels. In this process, 20 experiments were designed in order to achieve optimum conditions for heavy metal removal.

Environmental water analysis

Wastewater of copper factory was obtained from Sarcheshmeh city. The sample was filtered before the analysis and was applied according to the "Procedure of heavy metal removal by biosorbents" and "Procedure of heavy metal removal by SnO2 nanowires SPE (SNW-SPE)" sections.

Results and discussion

Preparation and characterization of SNW-SPE

Previously, SnO_2 nanowires were introduced by the thermal decomposition of tin chloride and ammonia via hydrothermal method (Lupan et al. 2007). To give an insight into the controlling shape and size of SnO_2 nanostructure, the researchers introduced the design of SnO_2 nanowires theoretically and practically. C.H. Yan reported the morphology of SnO_2 nanowires had been found to be dependent on the synthesis conditions. Shape, dimension and aspect ratio are functions of precursor concentration, growth time and Sn^{4+}/OH^{-} ratio (Lupan et al. 2009).

The result of SEM (Fig. 1a) of synthesized SnO_2 at 0.02 M concentration of tin chloride shows that the dominant structure is spherical particles. It seems, in this

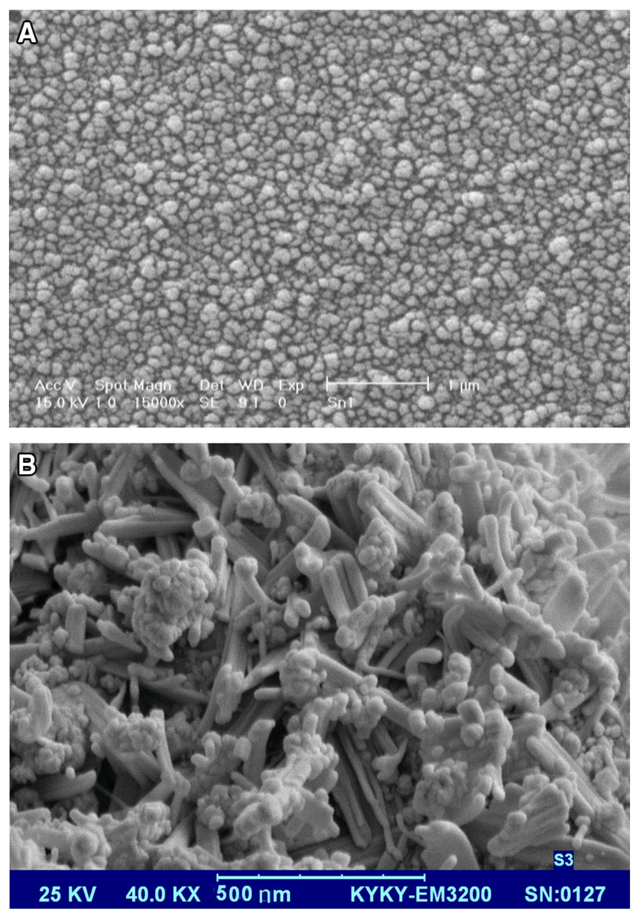

Fig. 1 SEM of synthesized SnO_2 at **a** 0.02 M, **b** 0.03 M concentration of tin chloride

condition that there is no sufficient growth solution for the growth of SnO_2 nanoparticles.

The aspect ratio of nanocrystals also gradually increases, followed by an increase in tin chloride concentration. Nanowires are formed when the concentration of tin chloride rises to 0.03 M (Fig. 1b). Investigation in the literature shows that the molar ratio of $SnCl_4$ to ammonia is an effective parameter on aspect ratio of nanowires (Lupan et al. 2009). The aspect ratio of SnO_2 nanowires augmented by raising the ratio of NH_4OH to $SnCl_4$ from 10:1 to 30:1. Experimental results in the laboratory indicated that appropriate molar ratio of NH_4OH to $SnCl_4$ for the growth of SnO_2 nanowires is 30:1. In addition, elevating the temperature and extending the heating time can also increase the aspect ratio of nanocrystals. Results of the experiments indicate that the growth process of nanowires is completed at 15 min and maximum available temperature is 98 °C. This temperature is under the boiling point of water solution. Finally, the SnO_2 nanowires were formed with 60–80 nm diameter and more than 1 µm length (Fig. 1b).

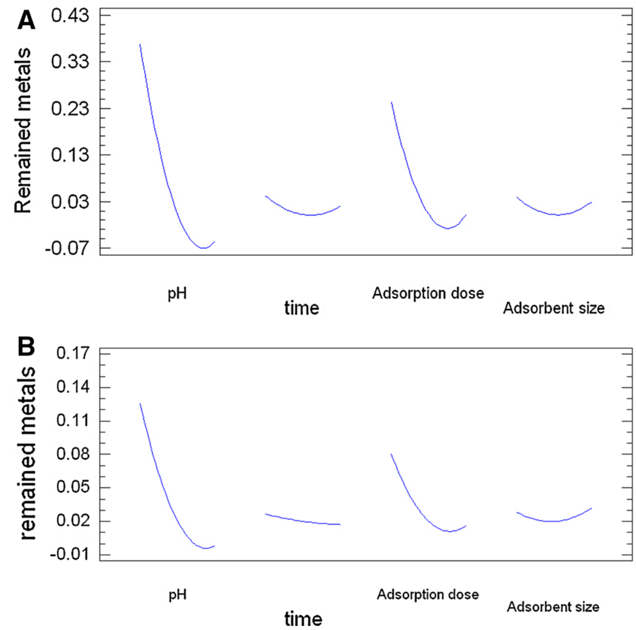

Fig. 2 Main effect of heavy metal removal from water by **a** pine core, **b** buttonwood fruits

Optimization parameters for removal of heavy metals from water

Removal of heavy metals by pine core and buttonwood fruit

Various parameters potentially affect the removal process. In order to remove selected heavy metals in a short period of time and with a high yield, these parameters have to be optimized. In this research, the optimum levels of significant factors were found by applying Box–Behnken and response surface methodology. The effect of four factors was investigated in three levels including adsorption dose of biosorbent (0.2–10 mg l^{-1}) (B), biosorbent size (>300, 250–150, <120 mm) (D), PH of solution of Pb(II) and Cu(II) (50 mg l^{-1}) (2–8) (A) and removal time (10–180 min) (C). The Box–Behnken method has been carried out on thirty randomized runs in three blocks and two repetitions of the center point in each block. The removal of heavy metals was performed by pine core powder and buttonwood fruit from 20 ml of heavy metals solution, separately. The remaining amounts of heavy metals were determined by atomic absorption spectroscopy, and it was selected as the response of designed experiments. To evaluate the main effect of each factor and interaction terms, analysis of variance (ANOVA) was used. The quality of fit of the model equation was represented by the coefficient of determination (R^2). R^2 of 0.928 for pine core and 0.919 for buttonwood fruit showed a good relationship between experimental data and fitted model at $p < 0.05$ level, as well as a potential of model in the prediction of response. Figure 2a and b shows the main effect parameters for the removal of heavy metals by pine core and buttonwood fruit.

The results indicate an increase in pH enhanced removal of heavy metal efficiency. At the acidic condition, H^+ competes with heavy metals ions for adsorption by biosorbent. Lower atomic diameter and higher ion mobility of H^+ than Pb^{2+} and Cu^{2+} cause it to be the winner in competition. On the other hand, metal hydroxides are formed at the base. So, increasing the pH to more than 7.5 decreased the removal efficiency of heavy metals.

The second parameter is biosorbent dose which affects the efficiency of heavy metal removal. Specific surface area of biosorbent was enhanced by increasing biosorbent dose; this causes a rapid removal of heavy metals by pine core and buttonwood fruit till 5.1 gl^{-1}(Fig. 2). No remarkable increase in the removal efficiency of heavy metals appeared after adding biosorbent dose up to more than 5.1 gl^{-1}. It may be the result of the aggregation of biosorbent powder.

Equilibrium time is a required parameter for the removal of heavy metal from water sample. The efficiency of heavy metal removal was enhanced by lengthening time, up to the equilibrium time. After that, back extraction process appeared and the remaining of heavy metals in water was proliferated.

The size of adsorbent is the last investigated parameter. It was observed that by decreasing the adsorbent particle size, the efficiency of heavy metal removal was improved. It is because of an increase in specific surface areas, related to the volume of absorbent particles. Hence, the best efficiency was achieved at the 250–150 mm (2) size. Furthermore, decreasing particle sizes to <120 mm showed a deficiency in removing of heavy metals from waters. This deficiency is due to the aggregation of adsorbent particles and the interaction of adsorbent size with other parameters (Fig. S_1 in the supplementary data). The removal results for Cu and Pb by pine core and buttonwood are the same. Hence, just the results of one of them are demonstrated. Table 1 shows the parameters domain and optimized conditions for removing Cu and Pb by pine core and buttonwood biosorbent.

Investigation of Pareto chart for Pb and Cu by pine core showed that the pH and adsorption dose have a negative effect on removing heavy metals from water, while the square of pH and adsorption dose have positive effect (Fig. S_{2a} in the supplementary data). Pareto chart of removing of Cu and Pb by buttonwood particles showed the pH and interaction of pH and adsorption dose (AC) are effective parameters on the removing process. The pH has negative effect, and interaction of adsorption dose with pH has positive effect (Fig. S_{2b} in the supplementary data).

Heavy metal removal by SnO_2 nanowires solid-phase extraction disk

The efficiency of heavy metal removal by SnO_2 nanowires SPE (SNW-SPE) depends strongly on the extraction parameter conditions. Experimental conditions such as pH (4–10), transfer rate of solution from SNW-SPE (1–3 ml min^{-1}) and initial concentration of heavy metal (10–90 mg l^{-1}) were optimized by Box–Behnken factorial design method. The normalized results of the experimental design were calculated at the 5% significance by the standardized Pareto chart. Results of the effective parameter estimation showed that the pH (A), pH square (AA) and interaction of pH and transfer rate (AB) are effective parameters on the process of removing heavy metals (Fig. 3). Cu and Pb removal from water by SNW-SPE showed the same results. Therefore, the graphs and curves were shown as heavy metals. Figure 4 illustrates the main effect of parameters. The results indicate that the increase in pH led to the decrease in heavy metal concentration from water till 8.5. The removal efficiency of heavy metals decreased after pH 8.5. It is due to the formation of metal hydroxide precipitate. The second parameter is the transfer rate of solution from SPE disk. Low transfer rate led to high interaction between metals and the surface of SNW-SPE. When transfer rate increased, the removal efficiency of heavy metals decreased. Metal concentration is the final optimized parameter. The main effect graph demonstrates that with increasing metal concentration, the efficiency of heavy metal removal decreased. It is clear that the absorption site on the SNW decreased rapidly with increasing metal concentration. A typical response surface function and the related contours for achievement of optimum condition for effective parameters on heavy metals removal efficiency are illustrated in Fig. 5.

The same optimum conditions were achieved for the removal of Cu and Pb from water by SNW-SPE. Table 2 indicates ranges of the selected parameters and optimum conditions.

Adsorption isotherms

In order to successfully represent the equilibrium adsorptive behavior, it is necessary to know a satisfactory description of the equation state between two phases of the adsorption system. The experimental data were fitted by two kinds of isotherms (Kiran and Kaushik 2008).

$$\text{Langmuir equation: } \frac{C_e}{q_e} = \frac{1}{q_o \cdot b} + \frac{C_e}{q_o} \qquad (1)$$

where q_e is the amount adsorbed at equilibrium (mg g^{-1}) and C_e is the equilibrium concentration of metal ions in solution (mg l^{-1}). The q_o is the measure of adsorption capacity under the experimental condition, and b is a constant related to the energy of adsorption.

The second equation is Freundlich equation.

$$\text{Freundlich equation: } \log q_e = \log K + \frac{1}{n} \log C_e \qquad (2)$$

where the q_e and C_e are like the Langmuir equation and n is indicative of bond energies between metal ion and adsorbent, and K is related to bond strength. The linearized Langmuir and Freundlich isotherms of Cu and Pb are presented in Fig. S_3 and S_4 in the supplementary data.

Table 1 Domain of parameters and optimum conditions of removal of Cu and Pb by pine core and buttonwood

Parameters	pH	Adsorption time (min)	Adsorption dose (mg l^{-1})	Adsorbent size
Domain of parameters	2–8	10–180	0.2–10	1–3
Optimum condition for pine core	7	120	5.1	2
Optimum condition for buttonwood	7.5	120	5.1	2

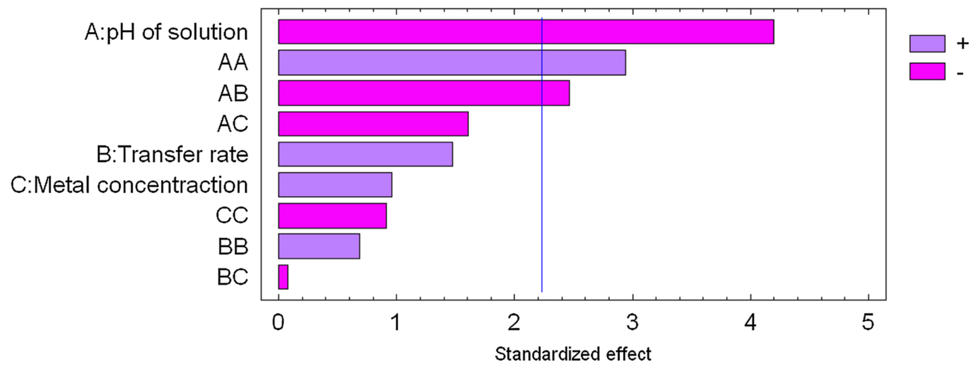

Fig. 3 Pareto chart of removing heavy metals from water by SNW-SPE

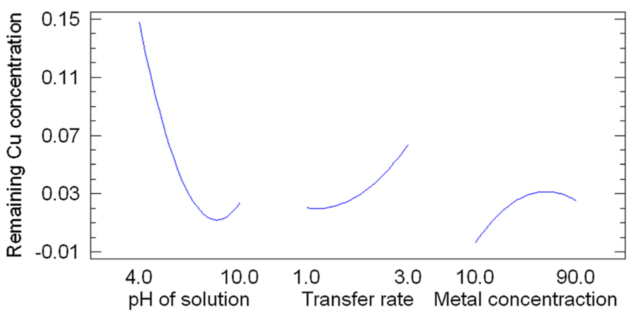

Fig. 4 Main effect of removing heavy metals from water by SNW-SPE

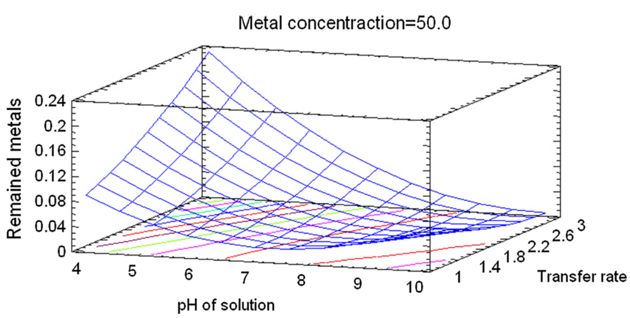

Fig. 5 Estimated response surface graph of removing heavy metals from water by SNW-SPE

Table 3 shows the estimated model parameters and correlation coefficient (R^2) for different models. The fitting of experimental data on the isotherms model was estimated by values of R^2.

Investigation of isotherms results shows the absorption of Cu and Pb by pine core, buttonwood and SNW-SPE was performed according to Langmuir model. It means that the heavy metals were adsorbed on the surface of sorbents.

Heavy metals removing efficiency

The removal efficiencies of heavy metals by three sorbents were calculated by Eq. 3:

$$R = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \tag{3}$$

where C_o and C_e are initial concentration and equilibrium concentration of heavy metals. The removing of heavy metals was performed at optimum conditions from a solution including 50 mg l^{-1} of Cu and pb. Table 4 shows the removal efficiency of heavy metals by three different sorbents.

The results show that the maximum removal efficiency of Cu was achieved by SNW-SPE, while these data for Pb was recorded by pine core. Also, the results show no remarkable difference between the removal efficiency of Pb by pine core and SNW-SPE. The advantages of SNW related to pine core and buttonwood sorbents are being recoverable by nitric acid and requiring low amount of sorbent in the removal process.

Interference of metal ions with the efficiency of removal of Cu and Pb from water

Interference of metal ions with the efficiency of Cu and Pb removal from water was estimated by five metal ions including Cr(VI), Mo(II), Fe(II), Ni(II) and Zn(II). Table 5 illustrates the results of the removing efficiency of Cu and Pb by pine core, buttonwood and SNW at the presence of interfered metal ions. Results indicate that this efficiency decreased in pine core sorbent. For buttonwood sorbent, interference of metal ions with the removal efficiency is less than that of pine core sorbent. Also, results show no remarkable decrease in the efficiency of Cu and Pb by

Table 2 Domain of parameters and optimum conditions of removal of Cu and Pb by SNW-SPE

Parameters	pH	Transfer rate (ml min^{-1})	Metal concentration (mg l^{-1})
Domain of parameters	4–10	1–4	10–90
Optimum condition for SNW-SPE	8.5	2.9	50

Table 3 Estimated isotherm models and their constants values for different types of adsorbents for lead and copper

Adsorbent type	Heavy metal	Langmuir equation			Freundlich equation		
		R^2	q_o	b	R^2	K	$1/n$
Pine core	Pb(II)	0.991	5.37	−1.91	0.926	1.37	0.465
	Cu(II)	0.997	7.75	−32.25	0.314	22.54	−0.514
Buttonwood	Pb(II)	0.975	5.88	−0.548	0.957	0.059	2.707
	Cu(II)	0.975	5.88	−0.55	0.747	897.02	−2.159
SNW-SPE	Pb(II)	0.962	3.29	4.47	0.957	3.24	0.484
	Cu(II)	0.930	2.78	6.41	0.784	2.897	0.413

Table 4 Removal efficiency of heavy metals by three types of adsorbents from standard solutions (St) and Sarcheshmeh copper factory wastewater (SCF)

Adsorbents	Removal efficiency of Cu (%)		Removal efficiency of Pb (%)	
	St	SCF	St	SCF
Pine core	98.72	61.32	99.62	88.29
Buttonwood	95.34	79.33	92.22	92.55
SNW-SPE	99.20	85.28	99.19	96.80

Table 5 Removal efficiency of heavy metals at the presence of interferences ions

Adsorbents	Removal efficiency of Cu (%)	Removal efficiency of Pb (%)
Pine core	75	54.42
Buttonwood	93.42	93.34
SNW-SPE	97.64	96.30

SNW removal. These results confirmed low interference of other metal ions on the removal efficiency of Cu and Pb by SNW-SPE. This is due to the existence of organic compounds in pine core and buttonwood sorbents. The organic compounds can form complex with metal ions and lead to a reduction in active sites of sorbents.

Removing of Cu and Pb by sorbent from copper factory wastewater

Removing of Cu and Pb from copper factory wastewater (20 ml) was performed by pine core, buttonwood and SNW-SPE at the optimum conditions. Table 4 indicates the results for Cu and Pb. The results show high deficiency for pine core and buttonwood sorbent. It is due to high interferences in the wastewater. Maximum removing efficiency was achieved by SNW-SPE. These results point out that the SNW sorbent has low interaction with interfering metal ions and other pollutants.

Conclusion

A rapid hydrothermal method was used for the synthesis of SnO_2 nanowires. The high aspect ratio was achieved by controlling ammonia and tin chloride concentration. The removal efficiency of SNW-SPE was compared with pine core and buttonwood as biosorbents. The results show higher removal efficiency of SNW-SPE than biosorbents. The advantages of SNW-SPE are low interference with other metal ions in the removal efficiency, reusability, ultrafast removal and high surface area. The adsorption behaviors of heavy metal ions onto the SNW-SPE, pine core and buttonwood match well with Langmuir isotherms. Using the SNW-SPE as adsorbent, economical wastewater treatment without SNW leakage into water is feasible. The SNW is promising materials for pre-concentration and solidification of heavy metal ions from large volumes of solutions.

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